TRANSLATION
of the European Patent Application 0 026 806

Fluorothermoplastic material including polytetrafluoroethylene admixture and a process for producing the same.

Fine-grained polytetrafluoroethylene (PTFE) is admixed in a pure form or filled with additives (compounds) to a thermoplastically processable fluoroplastic material and both components are melted in such a homogenous way that a thermoplastically processable mixed material having new properties is formed. PTFE advantageously comprises PTFE already sintered out and subsequently recycled into a fine-grained powder by comminuting, so-called reclaim. PTFE reclaim of compounds may contain a filling of known additives improving dry lubrication. The reclaim may further contain additives increasing the mechanical strength such as glass particles, minerals or metallic particles.

In the mixed material comprising PTFE particles which only very poorly wettable per se and not really thermoplastically fusable and a thermoplastically processable fluoroplastic material, especially perfluoroethylene-propylene (FEP) and perfluoroalkyl-perfluorovinylether and perfluoroalkoxyl (PFA and TFA), a real, almost homogenous bonding of PTFE with the ambient fusable matrix is formed. It is advantageous to continuously melt on the material being mixed and to carry out plastication during fusing on.

Fluorothermoplastic material including a polytetrafluoroethylene admixture and process for producing the same

It is the object of the invention to produce a thermoplastically processable fluoroplastic mixed material having new properties which contains homogenously distributed polytetrafluoroethylene (PTFE). It is the objective of this admixture to improve the mechanical strength values of the fluorothermoplastic material, to increase the permanent pressure stability and the abrasion resistance and to simultaneously reduce the friction coefficient so as to improve the sliding properties. Moreover, such admixture is interesting – and this is the case with the present prior art and/or the manufacturing prices -, when the mixed material found is more cost-efficient than the thermoplastically processable fluoroplastic and thus can be used more profitably.

This object was achieved by adding fine-grained, granulated or sintered PTFE. PTFE powders are granulated in general to improve the flow characteristics when filling pressing means, wherein granulating is frequently coupled with pre-sintering. PTFE already sintered out, thus production waste, is recycled by grinding into a fine-grained powder, wherein both unfilled (white) or filled PTFE types (referred to as compounds) are ground. These powders consisting of sintered PTFE are referred to as reclaim in plastics engineering, they are offered at lower prices than the original (juvenile) PTFE powder, as products made of reclaim in various respects result in more unfavorable PTFE qualities. For instance, tearing resistance, elongation at break, non-porosity, even structure, alternate bending strength and other properties are by far more unfavorable than those of the products made of juvenile PTFE. On the other hand, the pressure stability of PTFE products can be increased by adding reclaimed powder during production. Since PTFE as well as most fluorothermoplastic materials tend to flow when subjected to pressure and temperature, a reclaim additive may be advantageous in cases in which the permanent pressure stability is important, e.g. in packings or bearing inserts.

The addition of ground, cut or defibered, previously sintered PTFE into thermoplastic materials has been known long since. In bearing elements manufactured of thermoplastics including admixed PTFE the PTFE additive serves for reducing the

friction coefficient and/or the occurring PTFE abrasion serves as dry lubricant during sliding friction. It is known, for instance, according to US 29 75 128 and DE-PS 10 78 319 to embed PTFE particles in a thermoplastic matrix of polyamide, polystyrene, methyl methacrylate, cellulose butyrate or cellulose nitrate. In both patents the thermoplastic material liquefies at a temperature below the melting point of PTFE (327°C) and embeds the relatively coarse PTFE particles. It is stated in the cited US document that it is extremely difficult to produce a homogenous mixture of molten polyamide (nylon) and the PTFE particles; therefore it is suggested in that document to mix the fine-grained polyamide powder with the coarser PTFE particles in an unmelted condition, to press the mixture and to sinter the parts produced in this way at a temperature above the melting point of polyamide but below the melting point of PTFE.

In DE-PS 10 78 319 it is described that the PTFE particles having a preferred diameter of from 0.4 to 0.8 mm are suspended in the thermoplastic material at a temperature below the melting point of PTFE and injection-molded parts are manufactured of the mixture produced in this manner. In any case, the partly fused PTFE particles which do not combine with said plastic materials due to their anti-adhesive surface are merely embedded in the thermoplastics after solidifying.

GB-PS 96 70 87 claims as invention that bearing elements of polyamide, polyethylene or polyurethane are pressed with an admixture of particles of comminuted PTFE and said bearing elements having a low friction coefficient serve as inner sliding coatings of corresponding bearings. In this case, too, the foregoing is applicable to the bonding between PTFE and the thermoplastic matrix, because the melting point of said plastic materials is by far lower than that of PTFE.

Finally, DE-PS 12 95 808 and DE-AS 19 36 822 describe the manufacture of plastic molded parts in a casting process which in a thermoplastic matrix contain PTFE chips for reducing the sliding friction of bearing elements manufactured therefrom. One can take from these two prior publications, too, that the melting point of the thermoplastic matrix is by far lower than that of PTF, that the PTFE particles are only embedded in the matrix and have to be bonded, due to the missing wetting bonding between the

two matrices, by a particular shaping of the particles or by processes during cast resin manufacture.

In the present invention a completely different effect occurs. Between fluorothermoplastics and PTFE, e.g. especially between perfluoroethylene propylene (FEP) and perfluoroalkyl perfluorovinylether (perfluoroalkoxyl) (PFA and TFA), on the one hand, and PTFE, on the other hand, wetting of the PTFE occurs in the molten state. This wetting, too, which entails an extraordinarily tight bonding of the two surfaces is known already. The fluorothermoplastics FEP and PFA are used as welding means for connection between two PTFE parts that are not thermoplastically melting per se. Said welding methods were published already for FEP by DE-PS 95 29 97, for PFA by DE-AS 23 11 096, DE-OS 24 36 424 and DE-OS 25 21 734.

Now it has turned out that the wetting between PTFE particles that are not really thermoplastically fusable per se and PFA is extraordinarily good in the case of molten PFA whose temperature is above the melting point (gel point) of PTFE of 327°C. The two fluoroplastics similar as to their chemical structure and their specific weight (γ PTFE = 2.17, γ PFA = 2.14) combine in such a stable manner that no longer a suspension or dispersion is referred to but a homogenous mixed material. In this mixed material of two chemically related fluorothermoplastics the PTFE particles are no longer suspended but genuinely melted down, wherein a large surface of the PTFE admixture, i.e. a small grain size, is advantageous. When melting together thermoplastically processable fluoroplastics that are chemically related to PTFE with PTFE which is not thermoplastically processable, practically a fluoroplastic alloy exhibiting a number of surprising new product characteristics is formed.

For instance: good pressure stability mainly at higher temperatures and novel tensile strain behavior. The mixed material formed which, unlike the compositions mentioned in the described prior art, does not tend to separate, can be processed just like a homogenous thermoplastic material by thermal processes such as extrusion, injection molding, transfer molding and others.

By admixing ground PTFE in powder form to the PFA a mixed material having new physical and chemical properties is obtained, which in addition entails economic

advantages by the high manufacturing price of PFA and the low market price of PTFE reclaim. For example, the manufacture of mass-produced articles in an injection-molding process is basically cheaper than pressing them individually or manufacturing them of cast blanks by machining.

The method of admixing PTFE powder can also be used for the copolymer FEP related as to structure, wherein likewise a very good surface bonding takes place between PTFE particles and FEP thermoplastics. As, however, the characteristics of state of FEP differ already more strongly from those of PTFE, the bonding between these two components of the mixing material is not just as stable as it can be achieved with the combination of PFA-PTFE.

When using pure PFA (or TFA) for manufacturing bearing elements by injection molding, it is difficult when making use of these elements that the permanent pressure stability frequently is not sufficient. An admixture of fillers to PFA, e.g. of carbon or glass fibers, in order to increase the pressure stability deteriorates the friction coefficient of the material which in the case of pure PFA is already worse than with PTFE.

By admixing PTFE compounds, for example with a filling of coal, graphite, molybdenum disulphide or similar known admixtures having favorable dry lubricating properties as well as the mixtures thereof, both the pressure stability of the PFA-PTFE mixing material and its friction coefficient can be considerably improved. If only the pressure stability of PFA is to be increased, an admixture of PTFE compounds having a filling of glass in the form of fibers or balls, of metallic particles or mineral substances is recommended. Those PTFE compounds are known according to prior art.

It is still noted that in the current prior art PTFE compound waste is hardly used as reclaim, because the sintering properties thereof are very poor, the recycling results in products having unfavorable properties and thus practically no market exists for such waste. The powders of PTFE compound waste therefore can be prepared practically at the price of the grinding process.

The homogenous mixed material of a fluorothermoplastic and PTFE produced according to the invention can be adjusted depending on the requirements of purpose and nevertheless can be perfectly thermoplastically processed; it is similar to a homogenous alloy.

It has been found by tests that an admixture of up to 70 percent by weight of PTFE or PTFE compound to the PFA is possible, but that preferably an admixing share of PTFE between 15 and 40 % is used. The granularity of the ground PTFE advantageously is as fine as possible, for economic reasons in terms of comminution PTFE cannot be ground to any fine size. As tests have shown, the granularity of the PTFE powder should be as completely as possible below a grain diameter of 0.1 mm, wherein a large share of the granularity range is below 0.05 mm. In order to avoid separation, said PTFE powder is added in a dosed way, preferably directly to the PFA or FEP usually provided as granular material immediately before melt-on which commercially is executed mostly continuously. When the two components are jointly melted on, the extraordinarily good wetting between the fluorothermoplastics and PTFE is resulting so that, for instance, at the end of plastication in an extruder or an injection-molding machine an almost homogenous mixed material has been formed which exhibits the said novel advantages and properties.

As mentioned already, it has also been attempted and is known already to admix fillers in the form of glass fibers, coal, graphite or other fillers to PFA (or TFA), said admixture requiring a particular processing step, however. The PFA has to be melted on together with the fillers and then granulated, because if it is directly incorporated prior to the melting operation no homogenous mixture is formed between the two components due to the poor wetting ability. If the filler according to the invention is introduced along with the ground PTFE, however, a perfect compound which does not tend to separate is resulting, as a very good mutual wetting takes place between PTFE and the fluorothermoplastic substance.

Accordingly, it is stated that the invention achieves the object stated in the beginning, viz. to provide a new fluorothermoplastic mixed material having new properties which contains homogenously distributed PTFE, does not tend to separate and can be manufactured in an economically advantageous manner.

CLAIMS

1. A mixed material comprising a thermoplastically processable fluorothermoplastic with the addition of fillers, characterized in that fine-grained polytetrafluoroethylene (PTFE) has been added to the thermoplastically processable fluoroplastic material in pure form or filled with additives (compounds) and both components are fused homogenously so that a mixed material for further thermoplastic processing is formed.

2. A fluorothermoplastic mixture in accordance with claim (1), characterized in that ground, already sintered PTFE (reclaim) has been added as filler in pure non-filled form.

3. A fluorothermoplastic mixture in accordance with claim (1), characterized in that PTFE reclaim with a filling of coal, graphite, molybdenum disulphide and similar known additives improving dry lubrication, as well as mixtures thereof, has been added as filler.

4. A fluorothermoplastic mixture in accordance with claim (1), characterized in that PTFE reclaim powder having a filling of glass in the form of fibers or balls has been added as filler.

5. A fluorothermoplastic mixture in accordance with claim (1), characterized in that PTFE reclaim powder having a filling of mineral compounds or metallic particles has been added as filler.

6. A process for producing a mixed material comprising a fluorothermoplastic material of the perfluoroalkoxyl group (PFA or TFA) or perfluoroethylene propylene (FEP) and an addition of fillers, characterized in that powder or granular polytetrafluoroethylene (PTFE) of ground pure PTFE or PTFE compounds (reclaim) or a mixture of these two substances is added to the PFA or FEP thermoplastic material prior to or during fusing-on and that both components are jointly fused on.